

# Recent Developments in Anion Sensing Navigated by Thiourea-based Ligands: A Review

Adeeba Khan, Palak Dawar and Suranjan De\*

Department of Chemistry, Manipal University Jaipur, Rajasthan, India

## \*Correspondence to:

Suranjan De

Department of Chemistry,  
Manipal University  
Jaipur, Rajasthan, India.

E-mail: [suranjan.de@jaipur.manipal.edu](mailto:suranjan.de@jaipur.manipal.edu);  
[de.suranjan@gmail.com](mailto:de.suranjan@gmail.com)

Received: October 20, 2023

Accepted: December 22, 2023

Published: December 28, 2023

**Citation:** Khan A, Dawar P, De S. 2023. Recent Developments in Anion Sensing Navigated by Thiourea-based Ligands: A Review. *NanoWorld J* 9(S5): S505-S517.

**Copyright:** © 2023 Khan et al. This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CCBY) (<http://creativecommons.org/licenses/by/4.0/>) which permits commercial use, including reproduction, adaptation, and distribution of the article provided the original author and source are credited.

Published by United Scientific Group

## Abstract

The Multifunctional organosulfur compounds, such as thioureas and their derivatives, demonstrate numerous applications in biology, chemistry, and nanotechnology. The thiourea unit contains sulfur and nitrogen atoms, which exhibit nucleophilic characteristics and contribute to hydrogen bonding between a wide range of molecules, including various ionic species. The thiourea functional unit is useful as a chemosensor because of its distinctive chemical structure, which enables it to sense a variety of environmental contaminants. The several thiourea compounds and their synthetic analogues that are employed as sensitive and reliable fluorometric and colorimetric chemosensors are covered in this review article. Thioureas are mainly used to identify various cations, anions, as well as different neutral analytes. In biological, environmental, and agricultural environments, these applications are relevant. This review also describes and investigates the anion detecting capacities of thiourea-based chemosensors in detail. These discoveries may lead to the creation of advanced organic colorimetric and fluorescence sensors for the tracing of anions and neutral analytes. It is our aim that this thorough investigation encourages fresh ideas that eventually result in the development of chemosensors that are incredibly efficient, precise, and sensitive. The detection of many analytes in the disciplines of biology, chemistry, nanoscience, the environment, and agriculture could be considerably improved by these developments.

## Keywords

Thiourea, Chemosensor, Anion sensor, Colorimetric sensors, Fluorescence turn-on/off sensors, Nanosensor

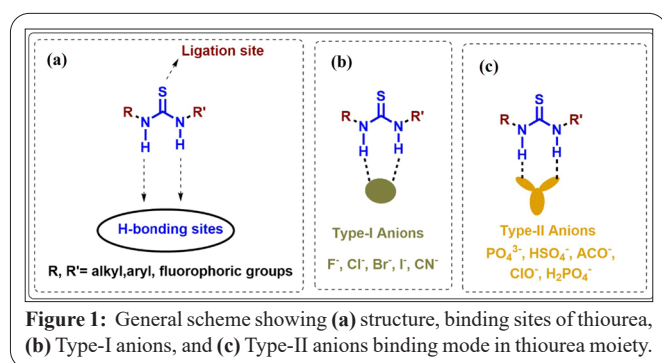
## Introduction

Environmental contamination caused by various ions, pesticides, medicines, and other hazardous chemicals is a major concern in the modern world [1, 2]. These pollutants cause a wide range of health issues, namely mental illnesses [3, 4], allergies [5, 6], oxidative tension [7, 8], kidney problems [9, 10], neurological disorders [11], infant mortality [12], endothelial malfunction [13], various cancers [14-16], and a variety of other detrimental effects. As a result, it is crucial to accurately identify these compounds, even at extremely low concentrations. Notably, distinct, sophisticated analytical techniques have been used therefore to locate these alarming compounds in extremely low quantities [17-25]. However, the methods frequently come at a high cost, call for labor-intensive sample preparation, and require complicated operational processes. Therefore, simple tools, very sensitive and extremely selective approaches to identify these contaminants in different samples at low levels are still in high demand.

Fluorometric and colorimetric sensors stand out among them as crucial methods for finding various kinds of environmental contaminants [26, 27].

These methods provide a straightforward, very sensitive, and selective way for identifying and detecting these dangerous chemicals in extremely low quantities. To focus on a range of analytes, several fluorometric and colorimetric chemosensors have been developed and manufactured [28-36]. Sensitivity and selectivity, as well as qualities like water solubility, perceptible color alteration, bright fluorescence shift, and a significant affinity for the target analyte, are all characteristics of an effective chemosensor. Chemosensors capitalize on a wide range of valuable interactions; cation/anion chelation and hydrogen-bond interactions are the most common among them. Therefore, the type of interactions that would be successful during the detection of a particular analyte is determined by the design of chemosensor units. Hence, the development of host-guest complex chemistry is essential for analyte detection, and careful host-guest component design has emerged as a key difficulty in modifying the chemosensor for a precise presentation of guest/host-binding activity. Today, a variety of techniques are being used to create the required binding components inside certain chemosensors.

Topics centred on nitrogen and sulfur have shown a wide range of applications within organic frameworks due to their adaptability and capacity for protonation and hydrogen bonding. Therefore, a notable example of such compounds with dual nitrogen and sulfur availability is the thiourea motif [37, 38]. Thiourea has the identical chemical structure as urea ( $\text{NH}_2\text{C}(\text{S})\text{NH}_2$ ), with the exception that an oxygen atom has been added in place of a sulfur atom (Figure 1a) [39]. Sulfur and nitrogen are both present in thiourea derivatives, giving them nucleophilic features that make it easier to form intra- and inter-molecular hydrogen bonds. Within the dominion of fluorescent and colorimetric chemosensors, the addition of thiourea provides a hydrogen-bonding unit, nurturing the construction of strong complexes that involve effective hydrogen bonding associations with biologically imperative ions [37]. Thus, thiourea derivatives are useful as organic sensors for the detection of various cation and anion-based environmental contaminants due to their nucleophilic characteristics and hydrogen bonding ability, which enable notable specificity and sensitivity while preserving affordability. Several derivatives of thiourea have been exploited for the detection and quantification of miscellaneous pollutants [39-40]. Excitingly, hydrogen atoms connected to the nitrogen atoms within thiourea units exhibit hydrogen bonds with halide ions, leading to the formation of six-membered ring structures (Figure 1b). On the contrary, when encountering oxo-anions, they produce eight-membered rings (Figure 1c)



**Figure 1:** General scheme showing (a) structure, binding sites of thiourea, (b) Type-I anions, and (c) Type-II anions binding mode in thiourea moiety.

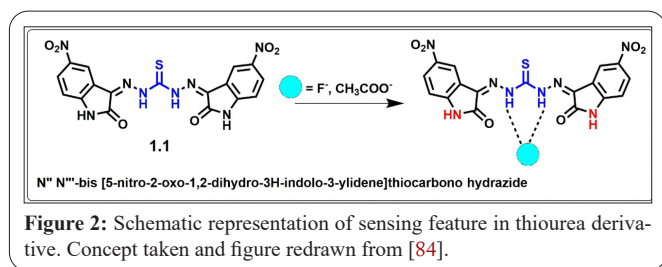
through hydrogen bonding [41]. Over the last few decades, a group of ligands with one or multiple thiourea units have been developed and exploited for the detection and sensing of anion and different toxic analytes [42-58].

An in-depth analysis of several thiourea compounds used as sensing materials for a range of anions across various media is the focus of this article. Additionally, a thorough evaluation of the sensing properties displayed by several thiourea derivatives is provided. This research intends to offer readers insightful information that will be useful for designing chemosensors and nanosensor based on thiourea compounds in future research.

## Thiourea Based Ligands for Anion Sensing

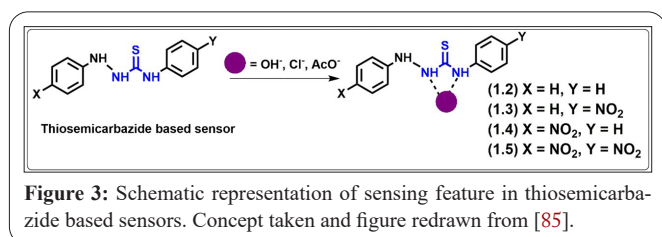
The invention and synthesis of new compounds that can precisely detect negatively charged species within an ion mixture fall under the category of anion recognition chemistry [59]. When ammonium cryptand receptors with positive charges were created for interacting with halides in the late 1960s, this field of study was born. Numerous charged/neutral molecules, organic and inorganic, both acyclic and cyclic, emerged as host systems as we moved deeper into the new century. These systems have been demonstrated to be competent in segregating, identifying, and forming complexes with anionic guest species in a specific and selective manner [60, 61]. Thiourea-based sensors have received substantial interest recently because of their variable binding qualities, sensitivity, and prospective uses in anion sensing and nanosensing [62]. Later, several sensors with exceptional degrees of sensitivity and selectivity for different anions were made public. Among others, they bind the ions namely cyanide ( $\text{CN}^-$ ), chloride ( $\text{Cl}^-$ ), hydroxide ( $\text{OH}^-$ ), sulfide ( $\text{S}^{2-}$ ), sulfate ( $\text{SO}_4^{2-}$ ), fluoride ( $\text{F}^-$ ), hydrogen sulfate ( $\text{HSO}_4^-$ ), carboxylate ( $\text{CO}_2^-$ ), acetate ( $\text{AcO}^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), nitrate ( $\text{NO}_3^-$ ), perchlorate ( $\text{ClO}_4^-$ ), citrate, and dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ) [63-71]. Hence, thiourea derivatives, as a tool, are important in the discipline of anion sensing for the precise determination of various anions. Numerous bonding possibilities with a variety of anionic species are provided by the addition of sulfur- and nitrogen-donor atoms [40].

Fluoride, or  $\text{F}^-$  ion, is a critical component for human health, playing a significant role in osteoporosis therapy, osteoporosis prevention, cancer prevention, bone development control, and the preservation of normal physiological processes [72-74]. However, consuming too much fluoride can cause major problems for some. It is generally acknowledged that constant exposure to high fluoride concentrations causes several illnesses, including skeletal fluorosis, dental fluorosis, declining birth rates, the risk of urolithiasis, bone fractures, cognitive development in children, and thyroid dysfunction [75-83]. As a result, it is crucial to create a chemosensor that is highly selective, efficient, sensitive, and economical. A chemosensor of this kind would be essential for precisely estimating fluoride amounts in various media. Therefore, in connection with that, Murali et al. [84] made a revolutionary discovery in 2014: a unique synthetic colorimetric sensor (Figure 2). This sensor was created by combining nitro-substituted indole and bis-thiocarbonohydrazone units. Their



objective was to detect  $F^-$  and  $AcO^-$  ions only. The researchers used ultraviolet-visible (UV-Vis) spectrophotometric titrations to determine the efficiency of this sensor in binding to these anions. The sensor's (**1.1**) absorption spectra in the solvent acetonitrile ( $CH_3CN$ ) exhibited a unique absorption band at 376 nm, resulting from the  $\pi-\pi^*$  electronic transition inside the framework of the sensor (**1.1**). Surprisingly, the distinctive absorption spectral intensity of compound **1.1** was significantly reduced when  $F^-$  and  $AcO^-$  anions were added. An absorption band for  $F^-$  ions developed at 515 nm and 506 nm for  $AcO^-$  ions, accompanied by a color transition from colorless to red. Using Job's plot analysis, the researchers discovered proof of receptor-anion complex development. In the complex production of fluoride ions, a 1:2 combination ratio was discovered, but a 1:1 combination ratio was detected for  $AcO^-$  ions. This result highlighted the promising ability of sensor (**1.1**) to recognize and specifically associate with these anions [84].

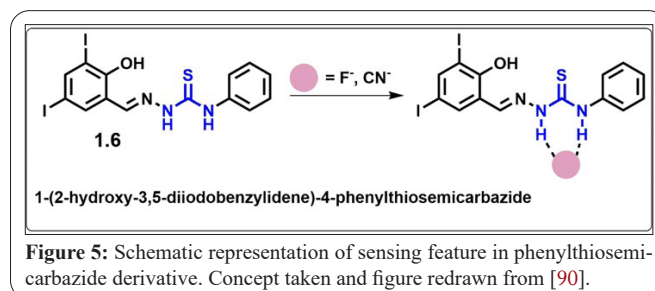
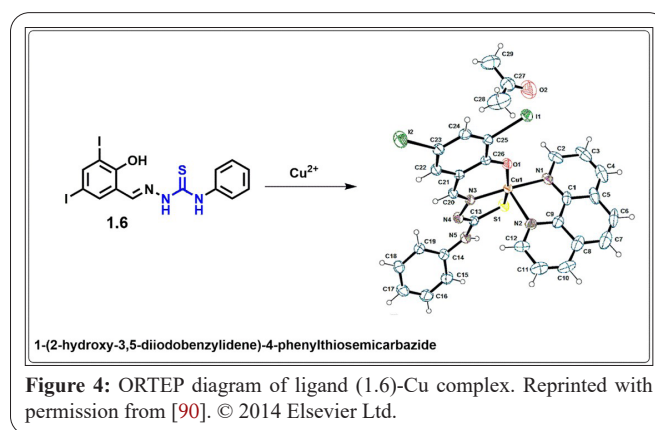
In the same year (2014), Farrugia et al. [85] synthesized thiosemicarbazide-based chemosensors (Figure 3) for anion identification. These chemosensors were created specifically to bind with ions such as  $OH^-$ ,  $F^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ , and  $Cl^-$ . Compound **1.2** stood out unique because it lacked a nitrophenyl electron withdrawing substituent, resulting in a shortage of absorbance in the range of 270 - 700 nm. When  $OH^-$ ,  $F^-$ , and  $AcO^-$  ions were added to compound (**1.2**), a wide shoulder appeared in its absorption spectra at about 335 nm. This transformation was followed by a modest shift in color from colorless to a mild yellowish tinge. However, the encounter of  $H_2PO_4^-$  and  $Cl^-$  ions with sensor had no influence on the absorption spectra. Compound (**1.3**), which included a 4-nitrophenyl substituent, showed a peak at 352 nm in a 9:1 dimethyl sulfoxide (DMSO)-water solvent combination. The band of absorption at 352 nm was reduced by the participation of the anions. A color changes from colorless to brown was also monitored. Compounds (**1.4** and **1.5**) had similar spectrum changes when  $OH^-$ ,  $F^-$ ,  $AcO^-$ , and  $H_2PO_4^-$  ions were introduced. Notably, these modifications were followed by significant hue shifts. Compound (**1.4**) went from colorless to purple, while compound **1.5** went from pink to reddish pink. The receptors, compounds (**1.2 to 1.5**), have



acidic characteristics that make them ideal for identifying anionic species. This recognition took place via directed hydrogen bonding or anion-induced deprotonation of the thiosemicarbazide functional group. These findings highlight the receptor's potential as a useful instrument for identifying and interacting with certain anionic species [85].

In addition to the  $F^-$  ion, cyanide can have a serious impact on the human respiratory, metabolic, vascular, central nervous system, endocrine, ocular, and pulmonary systems [86, 89]. Therefore, the discovery of a potential and selective chemosensor to check for an outbreak of  $CN^-$  ions is urgently required. Notably, in the same year (2014), Kumar et al. [90] established the preparation of a thiosemicarbazide based ligand and its four novel mononuclear mixed ligand  $Cu(II)$  complexes (Figure 4). Next, fluorescence staining studies were used to assess the cytotoxic activity of various complexes, indicating that the  $Cu$  complex containing phenazine derivative was the most potent.

The investigators also investigated the reaction of the ligand (**1.6**) to various anions using colorimetric experiments with various anions (Figure 5). When the ligand (**1.6**) was exposed to  $F^-$  and  $CN^-$  anions, noticeable color changes transpired. The encounter of the sensor with these anions,  $F^-$  and  $CN^-$ , was painstakingly examined using spectrophotometric methods. The receptor generated distinctive absorption peaks (at 250 nm, 325 nm, and 410 nm) in the absence of anions. These bands were most likely caused by intramolecular charge-transfer transitions that appeared throughout the Schiff base's structure. The absorbance peaks at 325 nm and 410 nm associated with the free ligand disappeared when  $F^-$  ions were introduced, resulting in complex formation with the receptor. In addition to that, a unique spectral band was developed at 490 nm. Surprisingly, identical spectrum alterations were seen when  $CN^-$  ions were added. The findings highlight the potential



of these manufactured complexes for a several applications, including cytotoxicity testing and the selective identification of certain anions by colorimetric and spectrophotometric methods [90].

In addition,  $F^-$  ions and  $AcO^-$  ions in high concentrations are hazardous not only to human health but also to aquatic creatures [91-94]. In the following year (2015), Saikia et al. [95] published two novel anion receptors (Figure 6). The researchers used UV-Vis spectroscopy to evaluate the detection and colorimetric sensing capabilities of receptors (1.7 and 1.8). When these receptors were subjected to anions like  $Cl^-$ ,  $NO_2^-$ ,  $N_3^-$ , etc., they displayed strong and specific binding with two anions, namely  $AcO^-$  and  $F^-$  ion. The researchers used density functional theory to explore how receptors (1.7 and 1.8) interacted with  $F^-$  and  $AcO^-$  anions in both  $CH_3CN$  solvent and gas phase to extract more information about the association processes. Different binding modalities were discovered by computer investigations. Receptor (1.7) established complexes by forming two intermolecular hydrogen bonds, whereas receptor (1.8) produced complexes via three intermolecular hydrogen bonds. Compared to receptor (1.7), receptor (1.8) showed a more dramatic change in electronic distribution before and after interaction with  $F^-$  and  $AcO^-$ . Job's plot assessment was also used in the study, which demonstrated the generation of a 1:1 complex between sensor (1.8) and  $F^-$  as well as with  $AcO^-$  ions [95]. These discoveries will contribute to a better apprehension of the binding characteristics and potential applications of them in newly discovered anion sensors.

$CN^-$  ion is widely recognized as a deadly anion that has devastating effects on human life. The smallest quantity of  $CN^-$  ion can attach to the active centre of cytochrome c, halting the activity of the mitochondrial electron transport chain and resulting in human death [86-90, 96]. In this regard, the development of specific and selective chemosensors to detect the existence of  $CN^-$  ions is greatly desired due to the nation's health consequences. Therefore, to generate a potential cyanide ion chemosensor, Suganya et al. [96] worked in 2015 to establish and investigate the different sensing capabilities associated with the  $CN^-$  ion in a 25% aqueous DMSO solution. They accomplished this by employing new heterocyclic-linked thiourea derivatives (Figure 7) with anthraquinone or phenazine as chromophore or fluorophore. The researchers utilized spectroscopic techniques such as UV-Vis, fluorescence, and proton nuclear magnetic resonance ( $^1H$  NMR) titration to inspect the distinct identification of the  $CN^-$  ion. The researchers also carried out colorimetric detection studies on a variety of anions ( $NO_3^-$ ,  $HSO_4^-$ ,  $F^-$ ,  $H_2PO_4^-$ , etc.). Surprisingly, the only significant change was seen in the reaction with  $CN^-$  ions. This change was seen as a bathochromic shift at 520 nm for compound (1.9) and 525 nm for compound (1.10). Whereas compounds (1.11 and 1.12) have dual absorption maxima at 402 and 420 nm, respectively. Furthermore, the interaction with  $CN^-$  ions gave rise to a characteristic absorption maximum at 495 nm for compounds 1.11 and 1.12, as well as a minor red shift to 427 nm for the existing band at 422 nm. The absorption spectra of the other examined anions stayed substantially constant. This

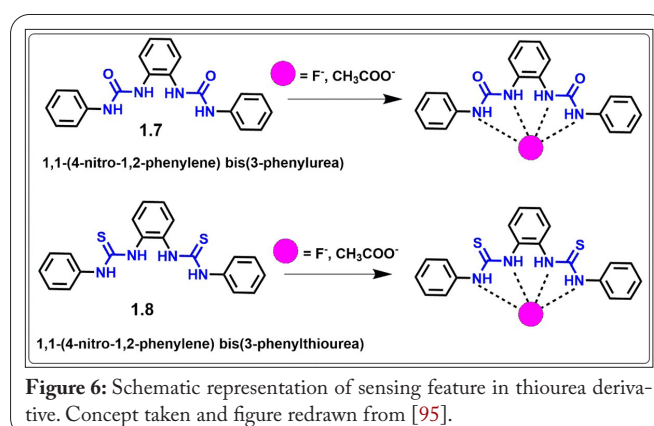


Figure 6: Schematic representation of sensing feature in thiourea derivative. Concept taken and figure redrawn from [95].

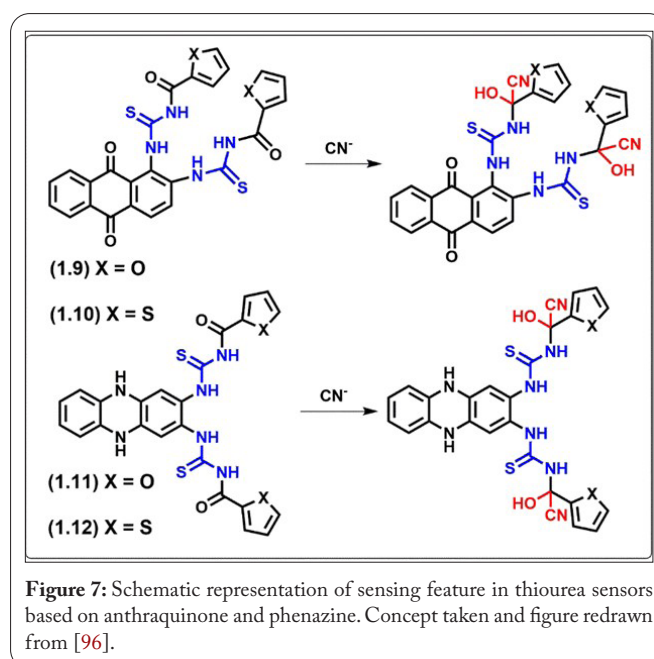


Figure 7: Schematic representation of sensing feature in thiourea sensors based on anthraquinone and phenazine. Concept taken and figure redrawn from [96].

significant bathochromic shift, as well as the evolution of a new absorption band, demonstrates the interaction of the highly acidic thiourea receptors (1.9 - 1.12) with the  $CN^-$  ion. Anions often engage receptors via hydrogen bonding, causing changes in electronic transitions. On the other hand, these receptors (1.9-1.12), were involved in nucleophilic substitution with the  $CN^-$  ion at the carbonyl functional group close to the furan or thiophene groups. Variations in the fluorescence intensity of (1.9 - 1.12) were predominantly driven by the formation of  $CN^-$  adducts. These changes in fluorescence intensity after  $CN^-$  ion exposure was ascribed principally to the production of  $CN^-$  adducts, followed by a sequential transfer of proton from the NH groups of the thiourea moiety. Through the analysis of Job's plot, it was understood that a 1:2 (receptors:  $CN^-$ ) complex formation has occurred. The addition of an anthraquinone chromophore allowed for simple colorimetric changes in response to the presence or absence of  $CN^-$  ions. This study shed light on the complicated processes behind the receptor's specific association with the  $CN^-$  ion, opening the way for future possibilities in ion detection and sensing [96].

$AcO^-$  ions in high concentrations are not only hazardous to phytoplankton and zooplankton but also have a serious impact on human health [91-94]. Hence, to generate a

unique thiourea-based sensor for selective detection of the  $\text{AcO}^-$  ion, Shang et al. [97] created four unique symmetrical chemosensors (Figure 8) in 2015 by combining anthracene or nitrobenzene with urea or thiourea groups. The researchers used spectrophotometric titrations in DMSO to examine the interactions of these four compounds with diverse anions such as  $\text{F}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{Cl}^-$ , etc. Among them, the urea derivatives showed modest spectrum responses when various anions were gradually added, indicating minimal host-guest interaction. When exposed to different anions, the thiourea derivatives containing nitrobenzene and anthracene displayed significant spectrum responses. Among the anions studied, the chemosensor (1.13) displayed outstanding sensitivity and selectivity in binding to  $\text{AcO}^-$  ions. The researchers also used fluorescence responses to investigate the binding properties of these anions. When  $\text{AcO}^-$  ions were sequentially added to the anthracene thiourea derivative, the emission intensity decreased significantly in contrast to the nitrobenzene derivatives. This fluorescence quenching was ascribed to a hydrogen bond blocking the excited-state intramolecular proton transfer activity on chemosensor (1.13) NH groups, after an intermolecular charge transfer phenomenon. Furthermore, the involvement of  $\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$  ions caused comparable alterations in the fluorescence emission spectra as with  $\text{AcO}^-$ . Among the anion-sensors produced, the anthracene derivative demonstrated outstanding effectiveness, which was linked to the conjugation activity of anthracene. According to Job-plot analysis, these spectrum changes were most likely caused by the creation of 1:1 host-guest complexes. This thorough analysis highlights the complex binding interactions and fluorescence responses displayed by these compounds while interacting with various anions, highlighting their potential applicability in sensing, and detecting fields [97].

To detect  $\text{F}^-$  anions more selectively, Yang et al. [98] in 2015 developed a set of colorimetric and fluorescence sensors that act as “On-Off” sensors based on diketopyrrolopyrrole (Figure 9). Compounds (1.14 - 1.17) were exhaustively tested for their ability to sense a range of anions, including  $\text{AcO}^-$ ,  $\text{F}^-$ ,  $\text{I}^-$ ,  $\text{HSO}_4^-$ ,  $\text{ClO}_4^-$ , etc. Compared to other anions, the binding assays demonstrated that these sensors had strong selectivity and precision for the  $\text{F}^-$  ion. Thiourea-based sensors (1.14 and 1.15) showed an increase of 78 nm in the wavelength in UV-Vis spectra when exposed to  $\text{F}^-$ , whereas urea-based sensors showed a larger increase in wavelength of 118 nm. When  $\text{F}^-$  ions were introduced, the fluorescence in sensors (1.14 - 1.17) was completely quenched. The deprotonation of the thiourea and urea moieties in reaction to  $\text{F}^-$  ions was linked to these spectrum shifts and alterations. Notably, there was a 1:4 bonding ratio between the receptors and the  $\text{F}^-$  ions. The limits of detection were established to be  $4.2 \times 10^{-8} \mu\text{M}$  for receptors (1.14 and 1.15) and  $2.5 \times 10^{-7} \mu\text{M}$  and  $3.4 \times 10^{-7} \mu\text{M}$  for receptors (1.16 and 1.17), respectively. The binding efficacy of thiourea receptors was larger than that of urea receptors, indicating that the former is more successful in building complexes with  $\text{F}^-$  ions [98].

In the following year, Yuan et al. [99] demonstrated a new azo-thiourea-based molecular tweezer (Figure 10) with

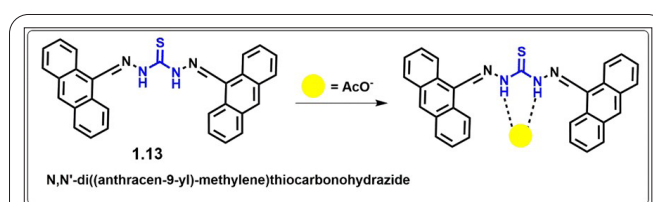


Figure 8: Schematic representation of sensing feature in thiocarbonylhydrazide derivative. Concept taken and figure redrawn from [97].

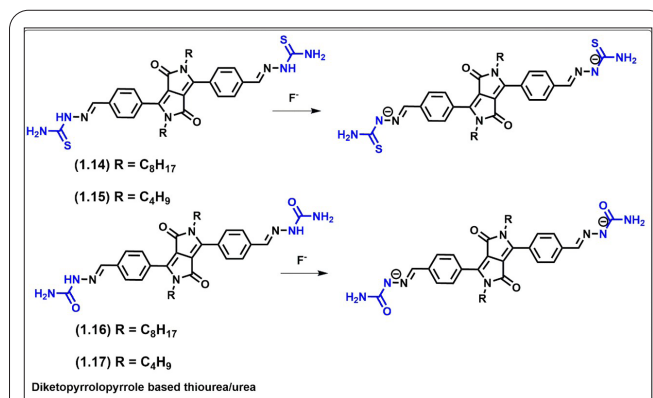


Figure 9: Schematic representation of sensing feature in thiourea based diketopyrrolopyrrole. Concept taken and figure redrawn from [98].

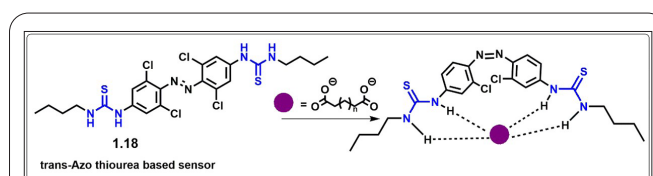


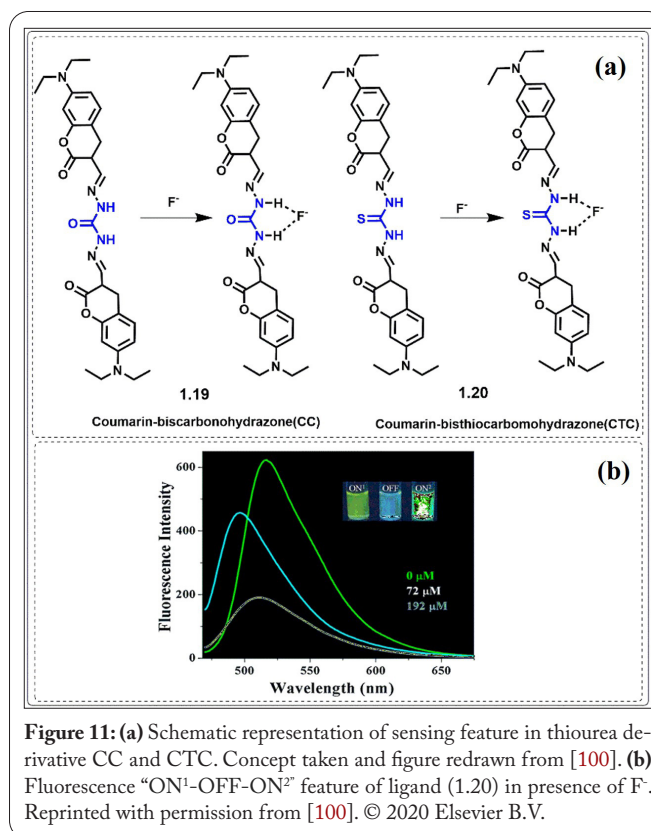
Figure 10: Schematic representation of sensing feature in azo-thiourea based sensor. Concept taken and figure redrawn from [99].

the capacity to selectively bind nonane dicarboxylate anions and azelate ions under visible-light induction. The researchers investigated the spectroscopic features and effectiveness of anion identification using rigorous titration tests with an array of anions. Compound (1.18) stood out among the receptors studied for its ability to preferentially bind bis-carboxylate anions. Furthermore, compound (1.18) demonstrated strong identification of azelate ions. The injection of these anions triggered a dramatic color alteration in the solution, emphasizing the coordination between the receptors and the anions. Importantly, the absorption spectra of the compound (1.18) were not altered by acetate, malonate, or succinate ions. Titrations of sensor (1.18) in DMSO with tetrabutylammonium salts of different anions, including  $\text{AcO}^-$ , other organic anions, were carried out. The compound's UV-Vis absorbance spectra and binding constants revealed unique alterations when the concentration of adipate and azelate ions was increased, distinguishing them from the rest. Surprisingly, all titrated anions displayed a 1:1 complex formation ratio, except for  $\text{AcO}^-$ , which exhibited a 1:2 stoichiometric binding. This study provided insight into compound (1.18)'s particular molecular interactions and binding choices, demonstrating its potential as a molecular tweezer with excellent selectivity for certain anions [99]. This type of research will add to our

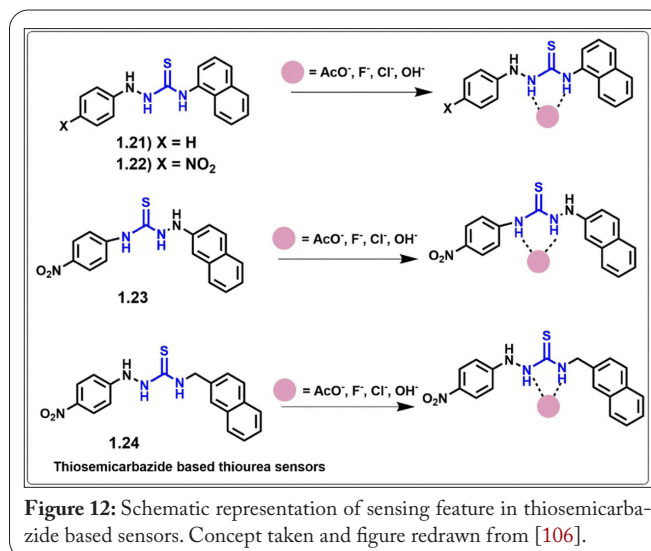
understanding of the further design and implementation of various anion sensors, revealing their ability to accurately and selectively sense anion concentrations.

In conjunction with an earlier report in the domain of  $F^-$  ion sensors, Biswas et al. [100] in 2016 proposed a new strategy by developing and synthesizing  $F^-$  ion receptors utilizing thiocarbohydrazone and carbohydrazone derivatives of coumarin (Figure 11) in a mixture of  $CH_3CN/DMSO$  solvent. The coumarin thiocarbohydrazone (CTC)-based receptor displayed significant discrimination and sensitivity to  $F^-$  ions, with a unique ON<sup>1</sup>-OFF-ON<sup>2</sup> fluorescence emission and visible colorimetric appearance. The detection method was explored employing UV-Vis and fluorescence spectroscopy as well as <sup>1</sup>H NMR titration investigations. The UV-Vis spectra of the chemosensors (1.19 and 1.20) were obtained in  $CH_3CN$  containing 0.25% DMSO, providing the following results: CTC showed an absorption maximum at 448 nm, indicating the  $n-\pi^*$  transition, as well as an additional peak near 278 nm, indicating the  $\pi-\pi^*$  transition. Colorimetric testing in  $CH_3CN$  was used to examine the association between both receptors and a variety of anions ( $F^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ , etc.). Notably, when the  $F^-$  ion met these receptors, it caused a significant color change, resulting in a light brown hue. Other anions, on the other hand, did not cause any apparent color change. Additionally, the  $F^-$  ion displayed a hypsochromic shift of 20 nm in fluorescence emission in a  $CH_3CN/DMSO$  solution, leading to a color change, i.e., the formation of cyan from green. The host-guest encounter between the receptors and  $F^-$  ions was linked to this distinct ON<sup>1</sup>-OFF-ON<sup>2</sup> activity. A thorough examination of Job's plot revealed that the coordination of CTC or CC with  $F^-$  took place in a 1:1 stoichiometry [100]. This kind of scientific practice will add to our understanding of the further design and implementation of  $F^-$  ion sensors, revealing their ability to sense anion concentrations accurately and selectively.

Hyperchloremia, or excessive chloride levels in the blood, can cause extreme dehydration, diarrhoea, or metabolic issues in which the blood becomes overly acidic, which leads to renal illness [101-105]. In the same year, Farrugia and coworkers developed a variety of thiosemicarbazide-based anion sensors (Figure 12) containing naphthalene and either 4-nitrophenyl or phenyl moieties. The compounds were analysed using different spectroscopic techniques. Furthermore, UV-Vis and fluorescence spectroscopy were exploited to investigate the anion detecting characteristics of compounds (1.21 - 1.24) in various solvent systems, including  $CH_3CN$ , DMSO, and  $H_2O/DMSO$  (1: 9 v/v).  $OH^-$ ,  $AcO^-$ , and  $Cl^-$  were among the anions targeted in their work. Among the studied compounds, 1.21 and 1.24 exhibited visible color differences in the presence of all anions except  $Cl^-$ , where the lack of a color shift was due to internal charge transfer events. A mechanistic approach including the deprotonation of the core-NH bond was postulated using proton, nitrogen, and various carbon NMR titration spectra, as well as density functional theory and charge distribution calculations. The compound (1.24) was purposefully developed with a methylene unit connecting the naphthalene and thiosemicarbazide segments to enhance photo-induced electron transfer [106].

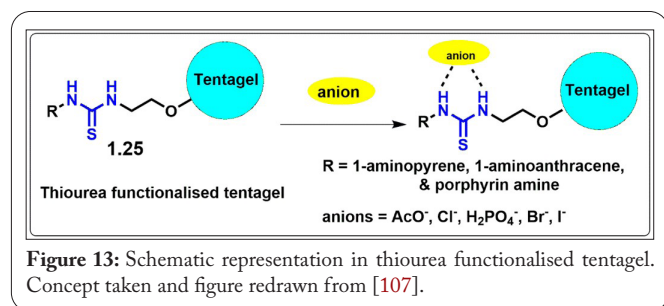


**Figure 11:** (a) Schematic representation of sensing feature in thiourea derivative CC and CTC. Concept taken and figure redrawn from [100]. (b) Fluorescence “ON<sup>1</sup>-OFF-ON<sup>2</sup>” feature of ligand (1.20) in presence of  $F^-$ . Reprinted with permission from [100]. © 2020 Elsevier B.V.



**Figure 12:** Schematic representation of sensing feature in thiosemicarbazide based sensors. Concept taken and figure redrawn from [106].

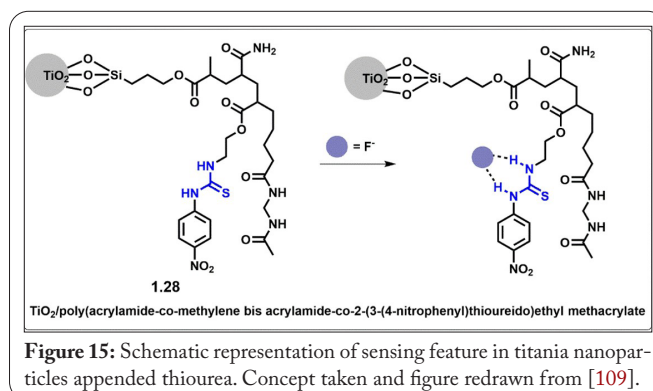
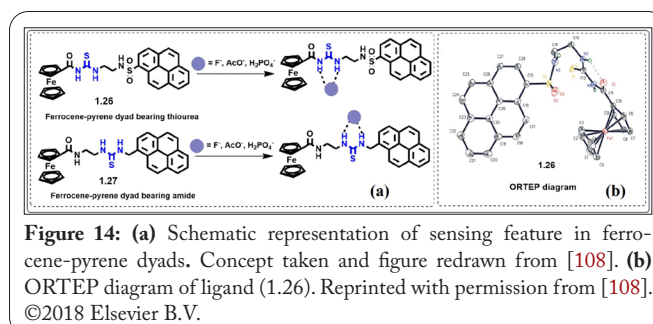
In the following year, Byrne and Mullen [107] conducted a study by developing an array of anion sensors using both urea and thiourea as the basis components. These sensors were investigated in solution as well as attached to polymer TentaGel resins (Figure 13). The first step was to convert 1-aminopyrene, 1-aminoanthracene, and porphyrin amine into their respective isothiocyanates, which were then reacted with TentaGel-NH<sub>2</sub> to produce surface-bound thiourea anion receptors. The observed chemical shift upon the addition of excess anions ( $AcO^-$ ,  $H_2PO_4^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ ) to anthracene and porphyrin receptors seemed to be smaller than that seen for urea sensors. Notably, anion binding was not studied using fluorescence emission due to the photodecomposition of receptors. Surprisingly, receptors functionalized with thiourea had a



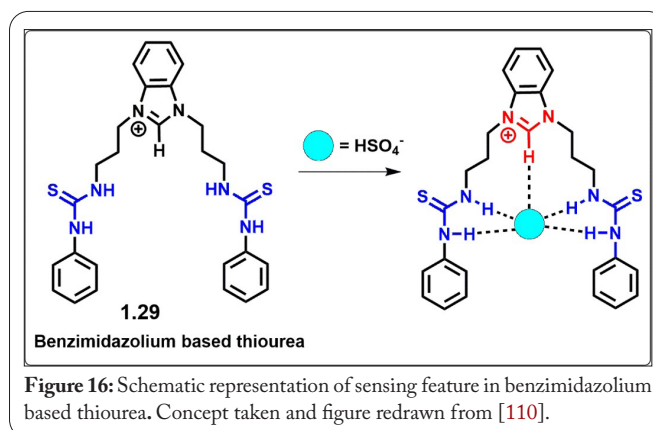
stronger affinity for anions ( $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ) except for halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ). This study emphasizes the customised creation of anion sensors and expands their applicability by incorporating them into polymer resins. The thorough comparison of urea and thiourea receptors reveals anion binding characteristics, enhancing our understanding of molecular interactions and possible applications in sensing [107]. This type of gel-based sensor will enhance our understanding of the further design and implementation of anion sensors, revealing their ability to sense anion concentrations accurately and selectively.

In the domain  $\text{F}^-$  ion sensor, Huang et al. [108] in 2018 developed two novel pyrene-appended ferrocene probes (Figure 14) linked by amide and thiourea units represented in an ORTEP diagram. These substances were thoroughly described, and their anion recognition characteristics were studied using electrochemical experiments and fluorescence methods. In  $\text{CH}_3\text{CN}$ , chemosensors (1.26 and 1.27) electrochemically detected  $\text{F}^-$ ,  $\text{AcO}^-$ , and  $\text{H}_2\text{PO}_4^-$  ions, resulting in a significant negative shift in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  potential. Additionally, fluorescence emission studies were carried out, indicating unique fluorescence quenching responses when exposed to  $\text{F}^-$  ions for both (1.26 and 1.27). The results of detailed fluorescence titrations revealed a 1:1 stoichiometric host-guest complexation between the probes and  $\text{F}^-$  ions. The compound's (1.26) detection limit for  $\text{F}^-$  ions was estimated to be  $1.59 \times 10^{-7} \mu\text{M}$ , whereas the compound's (1.27) detection limit was  $4.07 \times 10^{-7} \mu\text{M}$ . These results show not only the creation and characterization of new ferrocene-based compounds but also their promise as excellent anion sensors. The combination of electrochemical and fluorescence methods enabled a thorough knowledge of these compounds binding interactions and detection characteristics [108].

Nanoparticles with optical features such as chemiluminescence, fluorescence, and colorimetric responses have received a lot of interest. Exploiting these features of nanoparticles, in 2019, Sedghi and colleagues created a new colorimetric sensor (Figure 15) based on titanium nanoparticles appended with a thiourea moiety. The colorimetric analysis with numerous anions was explored, but a substantial color shift from pale yellow to orange was seen in the presence of the  $\text{F}^-$  ion, as well as a similar result with the addition of the acetate ion. When  $\text{F}^-$  is injected into the sensor, the UV-Vis experiment revealed the creation of a new band at 485 nm. The ratio of binding of  $\text{F}^-$  ion and receptor (1.28) through deprotonation of the thiourea group and H-bond formation between the  $-\text{NH}$  moiety was found to be 1:2. The lowest limit of detection for  $\text{F}^-$  was measured to be  $3 \mu\text{M}$  which shows the high selectivity of the sensor [109].



At high pH, hydrogen sulfate can break down to form toxic sulfate, causing irritation to the eyes and skin as well as paralytic breathing [67]. In the same year (2019), Bains et al. [110] developed, manufactured, and characterized a benzimidazolium-based thiourea receptor (Figure 16). The generated receptor (1.29) demonstrated outstanding sensitivity and selectivity for  $\text{HSO}_4^-$  ions when contrasted with other anions using commonly used spectroscopic techniques. The absorption band of the sensor (1.29), which was at 311 nm, moved to 261 nm when  $\text{HSO}_4^-$  ions were introduced, showing a substantial interaction between the receptor and the  $\text{HSO}_4^-$  ions. When excited at 310 nm, the sensor (1.29) emitted fluorescence at 455 nm. Notably, the steady addition of  $\text{HSO}_4^-$  ions led to a lessened emission peak at 455 nm as well as the arrival of a new emission maximum at 379 nm. The binding stoichiometry between compound (1.29) and  $\text{HSO}_4^-$  ions was shown to be a 1:1 complexation using extensive plot analysis. The receptor- $\text{HSO}_4^-$  complex's lowest detection limit was finalized to be 5.0 nM. Furthermore, the suggested sensor (1.29) demonstrated the capacity to detect  $\text{HSO}_4^-$  ions selectively in real-time aqueous sample analysis. This study not



only emphasizes the effective development and characterization of the benzimidazolium-based thiourea conjugate receptor but also demonstrates its potential application as a powerful and selective sensor for  $\text{HSO}_4^-$  ions, adding to the advancements made in anion detection approaches [110].

Viewing the current research importance of  $\text{F}^-$  ion sensing, Li et al. [111], in 2019 developed and synthesized two novel  $\text{F}^-$  ion probes/sensor (Figure 17). To investigate the binding properties of these probes using several anions, spectroscopic titrations with different anions in DMSO were performed. When  $\text{F}^-$  ions were introduced into the probe (1.30), a noticeable color variation of a purplish red color was noticed under visible light. Similarly, the inclusion of  $\text{F}^-$  ions caused the color of the sensor (1.30) solution to transition from light yellow to orange. Sensor (1.30) displayed two absorption maxima at 326 and 398 nm, which corresponded to  $\pi$ - $\pi^*$  electronic transitions. Only  $\text{F}^-$  ions caused a considerable bathochromic change, moving the absorption peak from 398 to 517 nm. The solution's color changed to purplish red in the presence of fluoride ion, suggesting a stable 1:1 interaction between  $\text{F}^-$  ions and the probe (1.30) to create a complex. Further research was also implemented to determine the reactivity of the sensor/probes in the presence of  $\text{F}^-$  and  $\text{OH}^-$ . An intriguing finding occurred when the concentration of  $\text{OH}^-$  ions was raised beyond 40 equivalents, resulting in the creation of a novel absorption graph. The interaction of  $\text{F}^-$  or  $\text{OH}^-$  as proton acceptors caused the removal of hydrogen from NH inside the thiourea moiety of probes (1.30 and 1.31), with excess  $\text{OH}^-$  constantly interacting with these receptors to produce new absorption bands. The lowest detection limits for probes (1.30 and 1.31) towards  $\text{F}^-$  ions were determined to be  $6.4 \times 10^{-8} \mu\text{M}$  and  $6.2 \times 10^{-8} \mu\text{M}$ , respectively. This study represented the effective design and development of innovative  $\text{F}^-$  ion probes, as well as insights into their behavior in the presence of various ions [111]. The observed reactions and interactions might open new possibilities for improved anion detection approaches.

$\text{F}^-$  and  $\text{AcO}^-$  ion sensing have become a common curiosity in the scientific community due to their hazardous nature. In the year 2019, Dey et al. [112] published another new tripodal benzoylthiourea chemosensor (Figure 18) anchored on tris (2-aminoethyl) amine. In aprotic liquids, this chemosensor revealed a colorimetric reflex to  $\text{F}^-$  and  $\text{AcO}^-$  ions. When fluoro-benzoylthiourea and N-benzamidobenzoylthiourea compounds were exposed to  $\text{AcO}^-$  and  $\text{F}^-$  ion, the presence of intramolecular hydrogen bonding was seen to decline. This difference was linked to the generation of hydrogen bonds between the receptor's (1.32) NH protons and corresponding anions. When  $\text{F}^-$  was added, a unique band appeared in the UV-Vis range at 315 nm, extending to higher wavelengths at 400 nm. In contrast, the addition of  $\text{AcO}^-$  caused the 315 nm peak to vanish, leaving only a tailing of the intramolecular charge transfer band towards 400 nm. However, other anions showed no appreciable spectrum shift in DMSO. Notably, due to their higher basicity than other anions,  $\text{F}^-$  and  $\text{AcO}^-$  were discovered to break intramolecular hydrogen bonds and form intermolecular hydrogen bonds with receptor (1.32). In aprotic solvents, this interaction triggered a colorimetric shift

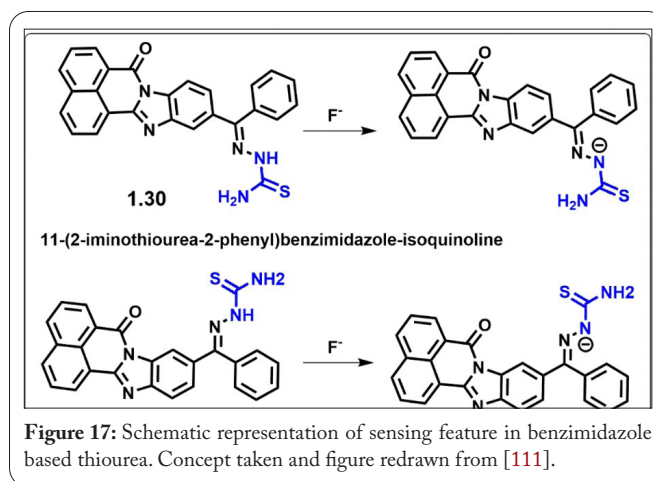


Figure 17: Schematic representation of sensing feature in benzimidazole based thiourea. Concept taken and figure redrawn from [111].

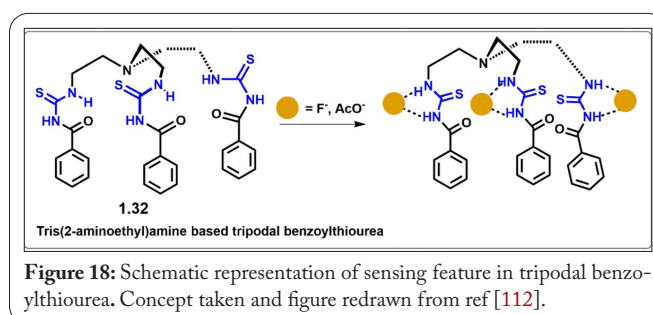


Figure 18: Schematic representation of sensing feature in tripodal benzoylthiourea. Concept taken and figure redrawn from ref [112].

from colorless to yellow. This research added to our knowledge of anion recognition and underlines the potential of the discovered receptor (1.32) for selectively identifying  $\text{F}^-$  and  $\text{AcO}^-$  ions, opening the possibilities for aprotic solvent-based colorimetric sensing applications [112].

Excess hypochlorite can cause several inflammatory disorders in the liver, kidneys, and lungs, as well as neurological problems [88]. In 2020, So et al. [113], and colleagues developed a fluorescent “turn-off” sensor (Figure 19) based on a thiourea framework for the detection of  $\text{ClO}^-$  ions. The interaction between  $\text{ClO}^-$  and chemosensor (1.33) resulted in a unique desulfurization mechanism inside the thiourea

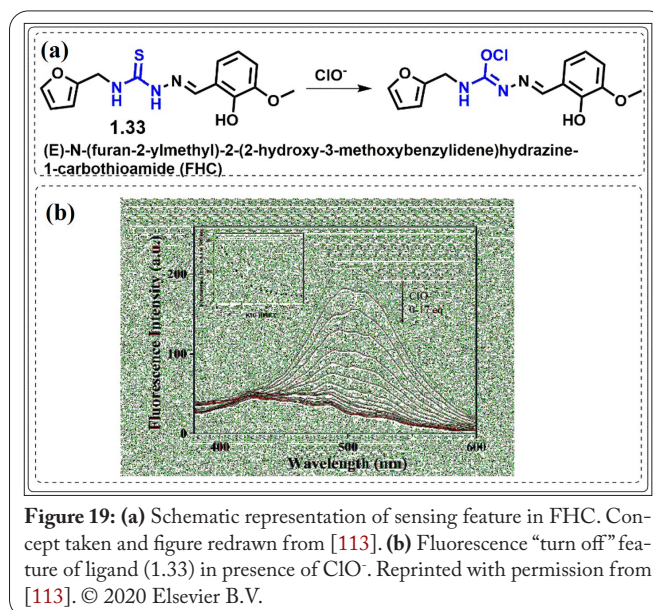


Figure 19: (a) Schematic representation of sensing feature in FHC. Concept taken and figure redrawn from [113]. (b) Fluorescence “turn off” feature of ligand (1.33) in presence of  $\text{ClO}^-$ . Reprinted with permission from [113]. © 2020 Elsevier B.V.

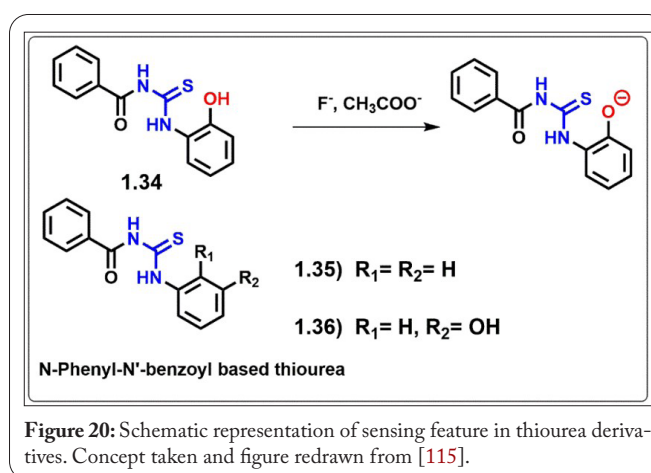


group, which reduced the fluorescence response. At 505 nm, compound (**1.33**) exhibited the most powerful fluorescence, which appeared as a brilliant green fluorescence hue. Surprisingly, except for  $\text{ClO}^-$  ions, none of the other analytes caused any apparent color changes in the sensor (**1.33**) spectra. The fluorescence “turn-off” reaction produced by  $\text{ClO}^-$  ions was extremely fast, happening in a matter of seconds. The reduction in fluorescence intensity at 505 nm revealed a linear association with the concentration of  $\text{ClO}^-$  ions, allowing the lowest detection limit of  $0.43 \mu\text{M}$  to be determined. The compound (**1.33**) was shown to be beneficial for imaging  $\text{ClO}^-$  ions in both HeLa cells and zebrafish, highlighting its potential for biological observation and sensing purposes [113].

Over time,  $\text{F}^-$  ion pollution in drinking water has been a worry for living organisms. In 2021, another  $\text{F}^-$  sensor was reported by Das et al. [114] and coworkers. In this study, Das and coworkers reported the synthesis of thiourea derivatives carrying a hydroxyl moiety (Figure 20) and detection of  $\text{F}^-$  ions aqueous medium. The results of anion binding experiments suggested that addition of  $\text{F}^-$  to the ligand (**1.34**) caused an obvious shift in color, from orange to crimson pale yellow, and the emergence of a new peak at 380 nm. In the presence of anions such as  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{CN}^-$ , sensors (**1.35** and **1.36**) similarly showed minor colorimetric changes. To inspect the influence of metal ions in the medium on anion recognition, these ligands were exposed to various metal ions, and anion sensing tests revealed that only **1.34** in the presence of  $\text{F}^-$  and  $\text{AcO}^-$  ions displayed significant colorimetric changes in the presence of metal ions (copper and nickel). The lowest limit of detection for  $\text{F}^-$  by sensor (**1.34**) was 2.47 ppm in DMSO, but 1.07 ppm and 1.9 ppm in the presence of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions, respectively [114].

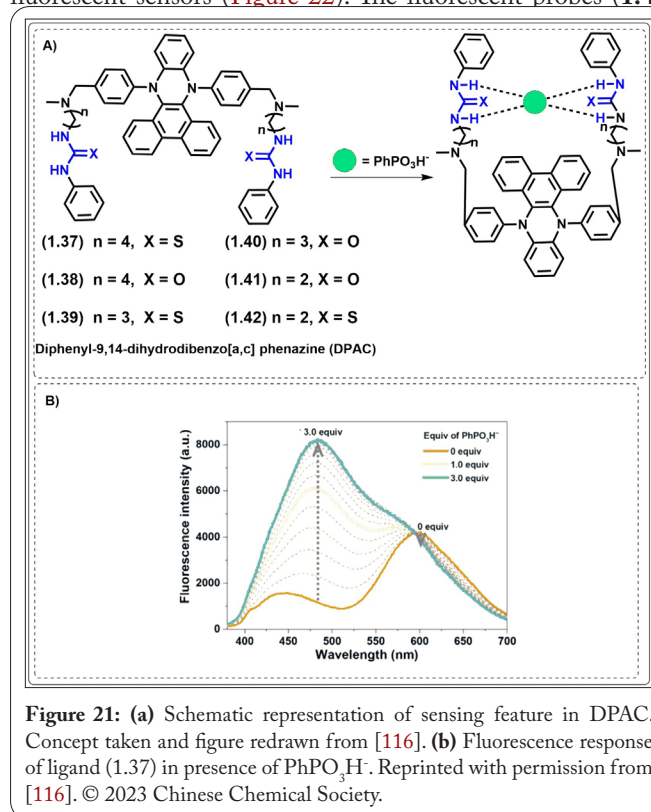
Phosphate in excess concentration can lead to artery hardening, inflammation, and cardiovascular disease [115, 116]. The investigation of fluorescence sensors for detecting small-molecule phosphates opens fascinating prospects for visually recognizing biorelevant processes and occurrences. However, due to the poor specificity of known phosphate receptors, differentiating phosphates from alternative anions such as  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions remains difficult. To address this, Zong et al. [116] in 2023 revealed the development of a flexible fluorescence sensor (Figure 21a) capable of distinguishing phosphates from comparable analogical anions. Their strategy was based on the exceptionally responsive conformation-dependent emission wavelengths of diphenyl-9,14-dihydrodibenzo[a,c]phenazine fluorophores. This technique allowed the sensor to detect small structural variations between phosphates and other similar anions like  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  with outstanding sensitivity (Figure 21b). It was also found that the designed chemosensor was able to detect the phosphate anion with the lowest detection limit of 94.4 nM [116].

High concentrations of  $\text{H}_2\text{PO}_4^-$  ions are linked to an elevated threat of heart disease and overall mortality rates [115, 117]. A high concentration of  $\text{H}_2\text{PO}_4^-$  can also cause a shortage of oxygen in the water and algal eutrophication [118]. In the same year (2023), Yang et al. [118] described

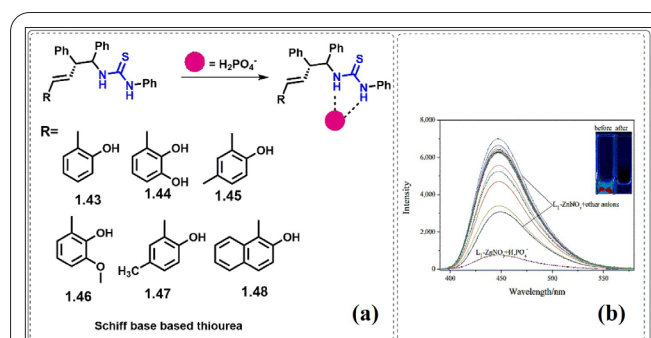


**Figure 20:** Schematic representation of sensing feature in thiourea derivatives. Concept taken and figure redrawn from [115].

the synthesis of an array of new chiral thiourea Schiff-base fluorescent sensors (Figure 22). The fluorescent probes (**1.43**



**Figure 21:** (a) Schematic representation of sensing feature in DPAC. Concept taken and figure redrawn from [116]. (b) Fluorescence response of ligand (**1.37**) in presence of  $\text{PhPO}_3\text{H}^-$ . Reprinted with permission from [116]. © 2023 Chinese Chemical Society.



**Figure 22:** (a) Schematic representation of sensing feature in thiourea Schiff base sensors. Concept taken and figures redrawn from [118]. (b) Fluorescence “turn off” feature of ligand (**1.43**) in presence of  $\text{H}_2\text{PO}_4^-$ . Reprinted with permission from [118]. © 2023 by the authors. Licensee MDPI, Basel, Switzerland.

- 1.48) demonstrated enhanced selectivity for  $Zn^{2+}$  in the presence of  $NO_3^-$  and were used as “turn-on” fluorescence probes for  $Zn^{2+}$ . Anion selectivity experiments were performed to explore the influence of various types of anions on zinc complexes. After excitation at 377 nm, the ligand (1.43) and  $Zn(NO_3)_2$  complex showed a high fluorescence emission maximum at 449 nm. On the other hand, when Zn complex of 1.43 were mixed with  $H_2PO_4^-$  ion, a color shift from brilliant blue to colorless was observed. In addition to that, when Zn complexes of all other ligands were mixed with  $H_2PO_4^-$ , similar alterations were seen. The generated complexes recognized  $H_2PO_4^-$  preferentially without interjection from other anions. The probe had an encouraging function and offered a novel practice for detecting  $Zn^{2+}$  and  $H_2PO_4^-$  in real samples [118].

These findings in this review will add to our understanding of molecular recognition and subsequently provide information for the creation of efficient anion-binding molecules. In addition to that, this study will enhance the reader's understanding of the further design and implementation of anion sensors, revealing their ability to sense anion concentrations accurately and precisely. Although it is clear from this review that the various thiourea-based chemosensors have been schemed and successfully utilized for biologically important ion sensing, yet the design and synthesis of very sensitive chemosensors may occasionally lack the required uniqueness. Notably, balancing selectivity and sensitivity remains a difficulty in the design of thiourea-based sensors. Additionally, transitioning from lab-scale investigations on chemosensors to practical usage necessitates resolving difficulties such as sample complexity and interference. It is also critical to ensure the sensor's stability over long periods of time, especially for outdoor usage. Therefore, new thiourea-based chemosensing approaches or practices for biologically important ions are still a competent area of research.

## Conclusion

In recent years, the use of chemosensor compounds has increased, owing to both the novelty of the concept and, more crucially, the operational simplicity and selectivity that they provide. Thiourea-based probes have proven to be useful tools for anion detection. According to the examples offered in this current review, thioureas have established their place as “booming” compounds in the development of chemosensor agents due to their capacity to deliver excellent chemosensing ability. Without a doubt, the next step is to create new thiourea-based ligands by improving their sensing features. On the other hand, modified thiourea chemosensors with increased binding and sensing capabilities are of significant interest to the scientific community. As a result, the colossal task is to develop novel structural characteristics in thiourea-based molecules with the potential to increase their involvement in chemosensing capabilities. It is believed that an increase in knowledge in the chemistry of small molecules would be propitious to the rational design of next-generation thiourea-based compounds that may be used for various applications in chemosensing and nanosensing.

## Acknowledgements

This work was sponsored by the Manipal University Jaipur, Rajasthan 303007. A.K and P. D are thankful to the Manipal University Jaipur for providing the doctoral scholarship. Authors are thankful Dr. M. Manna, Dr. A. Chakraborty, and Dr. A. Tarai for their help to collect research articles.

## Conflict of Interest

None.

## References

- Zhang XY, Lin FF, Wong MTF, Feng XL, Wang K. 2009. Identification of soil heavy metal sources from anthropogenic activities and pollution assessment of fuyang county, China. *Environ Monit Assess* 154: 439–449. <https://doi.org/10.1007/s10661-008-0410-7>
- Yuce G, Pinarbasi A, Ozcelik S, Ugurluoglu D. 2006. Soil and water pollution derived from anthropogenic activities in the pursuk river Basin, Turkey. *Environ Geol* 49: 359–375. <https://doi.org/10.1007/s00254-005-0072-5>
- Qiu H, Zhu X, Wang L, Pan J, Pu X, et al. 2019. Attributable risk of hospital admissions for overall and specific mental disorders due by particulate matter pollution China. *Environ Res* 170: 230–237. <https://doi.org/10.1016/j.envres.2018.12.019>
- Chen C, Liu C, Chen R, Wang W, Li W, et al. 2018. Ambient air pollution and daily hospital admissions for mental disorders in Shanghai, China. *Sci Bytal Environ* 613–614: 324–330. <https://doi.org/10.1016/j.scibytenv.2017.09.098>
- Behrendt H, Alessandrini F, Buters J, Kramer U, Koren H, et al. 2014. Environmental pollution and allergy: historical aspects. *Chem Immunol Allergy* 100: 268–277. <https://doi.org/10.1159/000359918>
- Lodovici M, Bigagli E. 2011. Oxidative stress and air pollution exposure. *J Byxicol* 2011: 487074. <https://doi.org/10.1155/2011/487074>
- Fiordelisi A, Piscitelli P, Trimarco B, Coscioni E, Iaccarino G, et al. 2017. The mechanisms of air pollution and particulate matter in cardiovascular diseases. *Heart Fail Rev* 22: 337–347. <https://doi.org/10.1007/s10741-017-9606-7>
- Xu X, Nie S, Ding H, Hou FF. 2018. Environmental pollution and kidney diseases. *Nat Rev Nephrol* 14: 313–324. <https://doi.org/10.1038/nrneph.2018.11>
- Kim H, Kim WH, Kim YY, Park HY. 2020. Air pollution and central nervous system disease: a review of the impact of fine particulate matter on neurological disorders. *Front Public Health* 8:575330. <https://doi.org/10.3389/fpubh.2020.575330>
- Sunyer J. 2008. The neurological effects of air pollution in children. *Eur Respir J* 32: 535–537. <https://doi.org/10.1183/09031936.00073708>
- Darrow LA, Woodruff TJ, Parker JD. 2006. Maternal smoking as a confounder in studies of air pollution and infant mortality. *Epidemiology* 17: 592–593. <https://doi.org/10.1097/01.ede.0000229951.26189.27>
- Sih T. 1999. Correlation between respiratory alterations and respiratory diseases due by urban pollution. *Int J Pediatr Obyrhinolaryngol* 49: S261–S267. [https://doi.org/10.1016/S0165-5876\(99\)00174-3](https://doi.org/10.1016/S0165-5876(99)00174-3)
- Byrnqvist H, Mills NL, Gonzalez M, Miller MR, Robinson S, et al. 2007. Persistent endothelial dysfunction in humans after diesel exhaust inhalation. *Am J Respir Crit Care Med* 176: 395–400. <https://doi.org/10.1164/rccm.200606-872OC>
- Zhao Y, Wang S, Aunan K, Martin Sei H, Hao J. 2006. Air pollution and lung cancer risks in China—a meta-analysis. *Sci Bytal Environ* 366: 500–513. <https://doi.org/10.1016/j.scibytenv.2005.10.010>
- Fernandez-Navarro P, Garcia-Perez J, Ramis R, Boldo E, Lopez-Abente G. 2017. Industrial pollution and cancer in Spain: an important pub-

- lic health issue. *Environ Res* 159: 555–563. <https://doi.org/10.1016/j.envres.2017.08.049>
16. García-Pérez J, Lope V, López-Abente G, González-Sánchez M, Fernández-Navarro P. 2015. Ovarian cancer mortality and industrial pollution. *Environ Pollut* 205: 103–110. <https://doi.org/10.1016/j.envpol.2015.05.024>
  17. Menzinger F, Schmitt-Kopplin P, Freitag D, Kettrup A. 2000. Analysis of agrochemicals by capillary electrophoresis. *J Chromatogr A* 891: 45–67. [https://doi.org/10.1016/S0021-9673\(00\)00567-7](https://doi.org/10.1016/S0021-9673(00)00567-7)
  18. Guo Z, Cai Q, Yang Z. 2005. Determination of glyphosate and phosphate in water by ion chromatography-inductively coupled plasma mass spectrometry detection. *J Chromatogr A* 1100: 160–167. <https://doi.org/10.1016/j.chroma.2005.09.034>
  19. Chen SH, Yang ZY, Wu H L, Kou HS, Lin SJ. 1996. Determination of thiocyanate anion by high-performance liquid chromatography with fluorimetric detection. *J Anal Byxicol* 20: 38–42. <https://doi.org/10.1093/jat/20.1.38>
  20. Wang F, Cao M, Wang N, Muhammad N, Wu S, et al. 2018. Simple coupled ultrahigh performance liquid chromatography and ion chromatography technique for simultaneous determination of folic acid and inorganic anions in folic acid tablets. *Food Chem* 239: 62–67. <https://doi.org/10.1016/j.foodchem.2017.06.016>
  21. Arienzo M, Capasso R. 2000. Analysis of metal cations and inorganic anions in olive oil mill waste waters by abymic absorption spectroscopy and ion chromatography. Detection of metals bound mainly by the organic polymeric fraction. *J Agric Food Chem* 48: 1405–1410. <https://doi.org/10.1021/jf990588x>
  22. Schmidt AC, Kutschera K, Mattusch J, Otby M. 2008. Analysis of accumulation, extractability, and metabolization of five different phenylarsenic compounds in plants by ion chromatography with mass spectrometric detection and by abymic emission spectroscopy. *Chemosphere* 73: 1781–1787. <https://doi.org/10.1016/j.chemosphere.2008.09.001>
  23. Hein R, Li X, Beer PD, Davis JJ. 2020. Enhanced voltammetric anion sensing at halogen and hydrogen bonding ferrocenyl SAMs. *Chem Sci* 2: 2433–2440. <https://doi.org/10.1039/d0sc06210c>
  24. Beer PD, Cadman J. 2000. Electrochemical and optical sensing of anions by transition metal-based receptors. *Coord Chem Rev* 205: 131–155. [https://doi.org/10.1016/S0010-8545\(00\)00237-X](https://doi.org/10.1016/S0010-8545(00)00237-X)
  25. Beer PD, Gale PA, Chen GZ. 1999. Mechanisms of electrochemical recognition of cations, anions, and neutral guest species by redox-active receptor molecules. *Coord Chem Rev* 185–186: 3–36. [https://doi.org/10.1016/S0010-8545\(98\)00246-X](https://doi.org/10.1016/S0010-8545(98)00246-X)
  26. Muhammad M, Khan S, Fayaz H. 2021. Charge-transfer complex-based spectrophotometric method for the determination of mesotriene in environmental samples. *Environ Monit Assess* 193: 1–7. <https://doi.org/10.1007/s10661-021-09432-0>
  27. Khan S, Chen X, Almahri A, Allehyani ES, Alhumaydhi FA, et al. 2021. Recent developments in fluorescent and colorimetric chemosensors based on schiff bases for metallic cations detection: a review. *J Environ Chem Eng* 9: 106381. <https://doi.org/10.1016/j.jece.2021.106381>
  28. Black CB, Andrioletti B, Try AC, Ruiperez C, Sessler JL. 1999. Dipyrrolylquinoxalines: efficient sensors for fluoride anion in organic solution. *J Am Chem Soc* 121: 10438–10439. <https://doi.org/10.1021/ja992579a>
  29. Lavigne JJ, Anslyn EV. 1999. Teaching old indicators new tricks: a colorimetric chemo sensing ensemble for tartrate/malate in beverages. *Angew Chem Int Ed* 38: 3666–3669. [https://doi.org/10.1002/\(SICI\)1521-3773\(19991216\)38:24%3C3666::AID-ANIE3666%3E3.0.CO;2-E](https://doi.org/10.1002/(SICI)1521-3773(19991216)38:24%3C3666::AID-ANIE3666%3E3.0.CO;2-E)
  30. Miyaji H, Saby W, Sessler JL. 2000. Naked eye detection of anions in dichloromethane: colorimetric anion sensors based on calix [4] pyrrole. *Angew Chem Int Ed* 39: 1777–1780. [https://doi.org/10.1002/\(SICI\)1521-3773\(20000515\)39:10%3C1777::AID-ANIE1777%3E3.0.CO;2-E](https://doi.org/10.1002/(SICI)1521-3773(20000515)39:10%3C1777::AID-ANIE1777%3E3.0.CO;2-E)
  31. Miyaji H, Sessler JL. 2001. Off the shelf colorimetric anion sensors. *Angew Chem Int Ed* 40: 154–157. [https://doi.org/10.1002/1521-3773\(20010105\)40:1%3C154::AID-ANIE154%3E3.0.CO;2-G](https://doi.org/10.1002/1521-3773(20010105)40:1%3C154::AID-ANIE154%3E3.0.CO;2-G)
  32. Piątek P, Jurczak J. 2002. A selective colorimetric anion sensor based on an amide group containing macrocycle. *Chem Commun* 20: 2450–2451. <https://doi.org/10.1039/B207335H>
  33. Anzenbacher P, Tyson DS, Jursiková K, Castellano FN. 2002. Luminescence lifetime-based sensor for cyanide and related anions. *J Am Chem Soc* 124: 6232–6233. <https://doi.org/10.1021/ja0259180>
  34. Xu G, Tarr MA. 2004. A novel fluoride sensor based on fluorescence enhancement. *Chem Commun* 9: 1050–1051. <https://doi.org/10.1039/B316121H>
  35. Sole S, Gabbai FP. 2004. A bidentate borane as colorimetric fluoride ion sensor. *Chem Commun* 11: 1284–1285. <https://doi.org/10.1039/B403596H>
  36. Kleerekoper M. 1998. The role of fluoride in the prevention of osteoporosis. *Endocrinol Metab Clin* 27:441–452. [https://doi.org/10.1016/S0889-8529\(05\)70015-3](https://doi.org/10.1016/S0889-8529(05)70015-3)
  37. Amendola V, Bonizzoni M, Esteban-Gomez D, Fabbrizzi L, Licchelli M, et al. 2006. Some guidelines for the design of anion receptors. *Coord Chem Rev* 250: 1451–1470. <https://doi.org/10.1016/j.ccr.2006.01.006>
  38. Duke RM, Veale EB, Pfeffer FM, Kruger PE, Gunnlaugsson T. 2010. Colorimetric and fluorescent anion sensors: an overview of recent developments in the use of 1,8 naphthalimide-based chemosensors. *Chem Soc Rev* 39: 3936–3953. <https://doi.org/10.1039/b910560n>
  39. Khan E, Khan S, Gul Z, Muhammad M. 2020. Medicinal importance, coordination chemistry with selected metals (Cu, Ag, Au) and chemosensing of thiourea derivatives: a review. *Crit Rev Anal Chem* 51: 1–23. <https://doi.org/10.1080/10408347.2020.1777523>
  40. Mohapatra RK, Das PK, Pradhan MK, El-Ajaily MM, Das D, et al. 2019. Recent advances in urea- and thiourea-based metal complexes: biological, sensor, optical, and corrosion inhibition studies. *Inorg Chem* 39: 127–187. <https://doi.org/10.1080/02603594.2019.1594204>
  41. Blazek Bregovic V, Basaric N, Mlinaric-Majerski K. 2015. Anion binding with urea and thiourea derivatives. *Coord Chem Rev* 295: 80–124. <https://doi.org/10.1016/j.ccr.2015.03.011>
  42. Sasaki SI, Citterio D, Ozawa S, Suzuki K. 2001. Design and synthesis of preorganized tripodal fluor receptors based on hydrogen bonding of thiourea groups for optical phosphate ion sensing. *J Chem Soc Perkin Trans 2*:2309–2313. <https://doi.org/10.1039/B105913K>
  43. Jiménez D, Marti nez-Mañez R, Sancenón F, Soby J. 2002. Selective fluoride sensing using colorimetric reagents containing anthraquinone and urea or thiourea binding sites. *Tetrahedron Lett* 43:2823–2825. [https://doi.org/10.1016/S0040-4039\(02\)00363-5](https://doi.org/10.1016/S0040-4039(02)00363-5)
  44. Jose DA, Kumar DK, Ganguly B, Das A. 2004. Efficient and simple colorimetric fluoride ion sensor based on receptors having urea and thiourea binding sites. *Org Lett* 6:3445–3448. <https://doi.org/10.1021/ol048829w>
  45. Jose DA, Kumar DK, Ganguly B, Das A. 2005. Urea and thiourea based efficient colorimetric sensors for oxyanions. *Tetrahedron Lett* 46: 5343–5346. <https://doi.org/10.1016/j.tetlet.2005.06.011>
  46. Kim YJ, Kwak H, Lee SJ, Lee JS, Kwon HJ, et al. 2006. Urea/thiourea-based colorimetric chemosensors for the biologically important ions: efficient and simple sensors. *Tetrahedron* 62: 9635–9640. <https://doi.org/10.1016/j.tet.2006.07.081>
  47. Ghosh K, Adhikari S. 2006. Colorimetric and fluorescence sensing of anions using thiourea based coumarin receptors. *Tetrahedron Lett* 47: 8165. <https://doi.org/10.1016/j.tetlet.2006.09.035>
  48. Kang J, Lee JH, Kim YK, Lee SK, Kim EY, et al. 2010. Simple urea/thiourea sensors for the biologically important ions. *J Incl Phenom Macrocycl Chem* 70: 29–35. <https://doi.org/10.1007/s10847-010-9853-x>

49. Li AF, Wang JH, Wang F, Jiang YB. 2010. Anion complexation and sensing using modified urea and thiourea-based receptors. *Chem Soc Rev* 39: 3729–3745. <https://doi.org/10.1039/b926160p>
50. Raposo MM, Acosta BG, Abalos T, Calero P, Martínez-Manez R, et al. 2010. Synthesis and study of the use of heterocyclic thiosemicarbazones as signaling scaffolding for the recognition of anions. *J Org Chem* 75: 2922–2933. <https://doi.org/10.1021/jo100082k>
51. Muhammad M, Khan S, Shehzadi SA, Gul Z, Al-Saidi HM, et al. 2022. Recent advances in colorimetric and fluorescent chemosensors based on thiourea derivatives for metallic cations: a review. *Dyes Pigments* 205: 110477. <https://doi.org/10.1016/j.dyepig.2022.110477>
52. Bhardwaj VK, Sharma S, Singh N, Hundal M, Hunda G. 2011. New tripodal and dipodal colorimetric sensors for anions based on tris/bis-urea/thiourea moieties. *Supramol Chem* 23:790–800. <https://doi.org/10.1080/10610278.2011.593629>
53. Moragues EM, Sanbys-Figueroa LE, Ábalos T, Sancenón F, Martínez-Mañez R. 2012. Synthesis of a new tripodal chemosensor based on 2,4,6-triethyl-1,3,5-trimethylbenzene scaffolding bearing thiourea and fluorescein for the chromo-fluorogenic detection of anions. *Tetrahedron Lett* 53:5110–5111. <http://dx.doi.org/10.1016/j.tetlet.2012.07.039>
54. Kado S, Otani H, Nakahara Y, Kimura K. 2012. Highly selective recognition of acetate and bicarbonate by thiourea-functionalised inverse opal hydrogel in aqueous solution. *Chem Commun* 49: 886. <https://doi.org/10.1039/c2cc3805>
55. Liu ZH, Devaraj S, Yang CR, Yen YP. 2012. A new selective chromogenic and fluorogenic sensor for citrate ion. *Sensors Actuators B* 174: 555–562. <http://dx.doi.org/10.1016/j.snb.2012.07.030>
56. Alaei P, Rouhani S, Gharanjiga K, Ghasem J. 2012. A new polymerizable fluorescent PET chemosensor of fluoride (F<sup>-</sup>) based on naphthalimide-thiourea dye. *Spectrochimica Acta Part A* 90: 85–92. <https://doi.org/10.1016/j.saa.2012.01.008>
57. Aldrey A, García V, Lodeiro C, Macías A, Pérez-Lourido P, et al. 2013. Colorimetric macrocyclic anion probes bearing nitrophenyl urea and nitrophenyl thiourea binding groups. *Tetrahedron* 69: 4578–4585. <https://doi.org/10.1016/j.tet.2013.04.016>
58. Kumar V. 2021. Urea/thiourea based optical sensors for basic analytes: a convenient path for detection of first nerve agent (Tabun). *Bull Chem Soc Jpn* 94: 309–326. <https://doi.org/10.1246/bcsj.20200285>
59. Chen L, Berry SN, Wu X, Howe ENW, Gale PA. 2020. Advances in anion receptor chemistry. *Chem* 6: 61–141. <https://doi.org/10.1016/j.chempr.2019.12.002>
60. Beer PD, Gale, PA. 2001. Anion recognition and sensing: the state of the art and future perspectives. *Angew Chem Int Ed* 40: 486–516. [https://doi.org/10.1002/1521-3773\(20010202\)40:3](https://doi.org/10.1002/1521-3773(20010202)40:3)
61. Gale PA. 2011. Anion receptor chemistry. *Chem Commun (Camb)* 47: 82–86. <https://doi.org/10.1039/c0cc00656d>
62. Soman S, PV A. 2021. Covalently modified graphene quantum dot using a thiourea based imprinted polymer for the selective electrochemical sensing of Hg (II) ions. *J Polym Res* 28: 359. <https://doi.org/10.1007/s10965-021-02716-6>
63. Keles E, Aydinler B, Nural Y, Seferoglu N, Sahin E, et al. 2020. A new mechanism for selective recognition of cyanide in organic and aqueous solution. *Eur J Org Chem* 2020: 4681–4692. <https://doi.org/10.1002/ejoc.202000342>
64. Nural Y, Keles E, Aydinler B, Seferoglu N, Atabey H, et al. 2021. New naphthoquinone-imidazole hybrids: synthesis, anion recognition properties, DFT studies and acid dissociation constants. *J Mol Liq* 327: 114855. <https://doi.org/10.1016/j.molliq.2020.114855>
65. Kubo Y, Kobayashi A, Ishida T, Misawa Y, James TD. 2005. Detection of anions using a fluorescent alizarin phenylboronic acid ensemble. *Chem Commun* 22: 2846–2848. <https://doi.org/10.1039/b503588k>
66. Gale PA, Caltagirone C. 2018. Fluorescent and colorimetric sensors for anionic species. *Coord Chem Rev* 354: 2–27. <https://doi.org/10.1016/j.ccr.2017.05.003>
67. Joo DH, Mok JS, Bae GH, Oh SE, Kang JH, et al. 2017. Colorimetric detection of Cu<sup>2+</sup> and fluorescent detection of PO<sub>4</sub><sup>3-</sup> and S<sup>2-</sup> by a multifunctional chemosensor. *Ind Eng Chem Res* 56: 8399–8407. <https://doi.org/10.1021/acs.iecr.7b01115>
68. Wei SC, Hsu PH, Lee YF, Lin YW, Huang CC. 2012. Selective detection of iodide and cyanide anions using gold nanoparticle-based fluorescent probes. *ACS Appl Mater Interfaces* 4: 2652–2658. <https://doi.org/10.1021/AM3003044>
69. Weng Y, Zhu Q, Huang ZZ, Tan H. 2020. Time-resolved fluorescence detection of superoxide anions based on an enzyme-integrated lanthanide coordination polymer composite. *ACS Appl Mater Interfaces* 12: 30882–30889. <https://doi.org/10.1021/acsami.0c09080>
70. Wang MQ, Li K, Hou TJ, Wu MY, Huang Z, et al. 2012. BINOL-based fluorescent sensor for recognition of Cu (II) and sulfide anion in water. *J Org Chem* 77: 8350–8354. <https://doi.org/10.1021/jo301196m>
71. Nawaz H, Zhang J, Tian W, Jin K, Jia R, et al. 2020. Cellulose-based fluorescent sensor for visual and versatile detection of amines and anions. *J Hazard Mater* 387: 121719. <https://doi.org/10.1016/j.jhazmat.2019.121719>
72. Bansal A, Ingle N, Kaur N, Ingle E. 2015. Recent advancements in fluoride: a systematic review. *J Int Soc Prev Community Dent* 5: 341–346. <https://doi.org/10.4103/2231-0762.165927>
73. Steiner DM, Steiner GG. 2004. Fluoride as an essential element in the prevention of disease. *Med Hypotheses* 62: 710–717. <https://doi.org/10.1016/j.mehy.2003.07.002>
74. Nielsen FH, Sandstead HH. 1974. Are nickel, vanadium, silicon, fluorine, and tin essential for man? a review. *Am J Clin Nutr* 27: 515–520. <https://doi.org/10.1093/ajcn/27.5.515>
75. Ozsvath DL. 2009. Fluoride and environmental health: A review. *Rev Environ Sci Biotechnol* 8: 59–79. <https://doi.org/10.1007/s11157-008-9136-9>
76. Whitford GM. 1992. Acute and chronic fluoride toxicity. *J Dent Res* 71: 1249–1254. <https://doi.org/10.1177/00220345920710051901>
77. Barbier O, Arreola-Mendoza L, Del Razo LM. 2010. Molecular mechanisms of fluoride toxicity. *Chem Biol Interact* 188: 319–333. <https://doi.org/10.1016/j.cbi.2010.07.011>
78. Dharmaratne RW. 2019. Exploring the role of excess fluoride in chronic kidney disease: a review. *Hum Exp Biomed* 38: 269–279. <https://doi.org/10.1177/0960327118814161>
79. Freni SC. 1994. Exposure by high fluoride concentrations in drinking water is associated with decreased birth rates. *J Bioclimol Environ Health* 42: 109–121. <https://doi.org/10.1080/15287399409531866>
80. Barberio AM, Hosein FS, Quinonez C, McLaren L. 2017. Fluoride exposure and indicators of thyroid functioning in the Canadian population: implications for community water fluoridation. *J Epidemiol Community Health* 71: 1019–1025. <https://doi.org/10.1136/jech-2017-209129>
81. Krishnamachari KAVR. 1986. Skeletal fluorosis in humans: a review of recent progress in the understanding of the disease. *Progr Food Nutr Sci* 10: 279–314. [https://doi.org/10\(3-4\):279-314](https://doi.org/10(3-4):279-314)
82. DenBesten P, Li W. 2011. Chronic fluoride toxicity: dental fluorosis. *Monogr Oral Sci* 22: 81–96. <https://doi.org/10.1159/000327028>
83. Li Y, Liang C, Slemenda CW, Ji R, Sun S, et al. 2001. Effect of long-term exposure by fluoride in drinking water on risks of bone fractures. *J Bone Miner Res* 16: 932–939. <https://doi.org/10.1359/jbmr.2001.16.5.932>
84. Murali M, Vishnumurthy KA, Seethamraju S, Ramamurthy P. 2018. Colorimetric anion sensor based on receptor having indole- and thiourea-binding sites. *RSC Adv* 4(39): 20592–20598. <https://doi.org/10.1039/c4ra01555j>
85. Farrugia KN, Makuc D, Podborska A, Szaciłowski K, Plavec J, et al. 2015. UV-Visible and 1H-15N NMR spectroscopic studies of colorimetric thiosemicarbazide anion sensors. *Org Biomol Chem* 13 (6): 1662–1672. <https://doi.org/10.1039/c4ob02091j>

86. Nelson L. 2006. Acute cyanide toxicity: mechanisms and manifestations. *J Emerg Nurs* 32: 8–11. <https://doi.org/10.1016/J.JEN.2006.05.012>
87. Egekeze JO, Oehme FW. 1980. Cyanides and their toxicity: a literature review. *Veterinary Quarterly* 2: 104–114. <https://doi.org/10.1080/01652176.1980.9693766>
88. Hamel J. 2011. A review of acute cyanide poisoning with a treatment update. *Crit Care Nurse* 31: 72–82. <https://doi.org/10.4037/ccn2011799>
89. Xu Z, Chen X, Kim HN, Yoon J. 2010. Sensors for the optical detection of cyanide ion. *Chem Soc Rev* 39: 127–137. <https://doi.org/10.1039/b907368j>
90. Kumar M, Dhahagani K, Rajesh J, Anitha K, Chakkaravarthi G, et al. 2015. Synthesis, structural analysis and cybybyxic effect of copper (II)-thiosemicarbazone complexes having heterocyclic bases: a selective naked eye sensor for F<sup>-</sup> and CN<sup>-</sup>. *Polyhedron* 85: 830–840. <https://doi.org/10.1016/j.poly.2014.09.044>
91. Hilderbrand DC, Der R, Griffin WT, Fahim MS. 1973. Effect of lead acetate on reproduction. *Am J Obstet Gynecol* 115: 1058–1065. [https://doi.org/10.1016/0002-9378\(73\)90554-1](https://doi.org/10.1016/0002-9378(73)90554-1)
92. Ozmen M, Yurekli M. 1998. Subacute toxicity of uranyl acetate in Swiss-albino mice. *Environ Byxicol Pharmacol* 6: 111–115. [https://doi.org/10.1016/S1382-6689\(98\)00025-8](https://doi.org/10.1016/S1382-6689(98)00025-8)
93. McGinty D, Vitale D, Letizia CS, Api AM. 2012. Fragrance material review on benzyl acetate. *Food Chem Byxicol* 50: S363–S384. <https://doi.org/10.1016/j.fct.2012.02.057>
94. Letizia CS, Cocchiara J, Lalko J, Api AM. 2003. Fragrance material review on linalyl acetate. *Food Chem Byxicol* 41: 965–976. [https://doi.org/10.1016/S0278-6915\(03\)00014-0](https://doi.org/10.1016/S0278-6915(03)00014-0)
95. Saikia E, Borpuzari PM, Chetia B, Kar R. 2016. Experimental and theoretical study of urea and thiourea based new colorimetric chemosensor for fluoride and acetate ions. *Spectrochim Acta Part A Mol Biomol Spectrosc* 152: 101–108. <https://doi.org/10.1016/j.saa.2015.07.065>
96. Suganya S, Velmathi S. 2015. Fluorogenic and chromogenic heterocyclic thiourea: selective recognition of cyanide ion via nucleophilic addition reaction and real sample analysis. *Sensors Actuabys B Chem* 221: 1104–1113. <https://doi.org/10.1016/j.snb.2015.07.059>
97. Shang X, Yang Z, Fu J, Zhao P, Xu X. 2015. The synthesis and anion recognition property of symmetrical chemosensors involving thiourea groups: theory and experiments. *Sensors* 15 (11): 28166–28176. <https://doi.org/10.3390/s151128166>
98. Yang X, Zheng L, Xie L, Liu Z, Li Y, et al. 2015. Colorimetric and on-off fluorescent chemosensor for fluoride ion based on diketopyrrolopyrrole. *Sensors Actuabys B Chem* 207 (Part A): 9–24. <https://doi.org/10.1016/j.snb.2014.10.095>
99. Yuan YX, Wang L, Han YF, Li FF, Wang HB. 2016. A novel azo-thiourea based visible light switchable anion receptor. *Tetrahedron Lett* 57(8): 878–882. <https://doi.org/10.1016/j.tetlet.2016.01.037>
100. Biswas S, Gangopadhyay M, Barman S, Sarkar J, Singh NDP. 2016. Simple and efficient coumarin-based colorimetric and fluorescent chemosensor for f<sup>-</sup> detection: an ON1-OFF-ON2 fluorescent assay. *Sensors Actuabys B Chem* 222: 823–828. <https://doi.org/10.1016/j.snb.2015.08.090>
101. Hostynek JJ, Patrick E, Younger B, Maibach HI. 1989. Hypochlorite sensitivity in man. *Contact Dermatitis* 20: 32–37. <https://doi.org/10.1111/j.1600-0536.1989.tb03092.x>
102. Ohnshin S, Murata M, Kawanishi S. 2002. DNA damage induced by hypochlorite and hypobromite with reference by inflammation-associated carcinogenesis. *Cancer Lett* 178: 37–42. [https://doi.org/10.1016/S0304-3835\(01\)00812-6](https://doi.org/10.1016/S0304-3835(01)00812-6)
103. Slaughter RJ, Watts M, Vale JA, Grieve JR, Schep LJ. 2019. The clinical toxicology of sodium hypochlorite. *Clin Byxicol (Phila)* 57: 303–311. <https://doi.org/10.1080/15563650.2018.1543889>
104. Panasenko OM, Sergienko VI. 2001. Hypochlorite, oxidative modification of plasma lipoproteins, and atherosclerosis. *Bull Exp Biol Med* 131: 407–415. <https://doi.org/10.1023/A:1017926309665>
105. Pan B, Ren H, Lv X, Zhao Y, Yu B, et al. 2012. Hypochlorite-induced oxidative stress elevates the capability of HDL in promoting breast cancer metastasis. *J Transl Med* 10: 1–13. <https://doi.org/10.1186/1479-5876-10-65>
106. Farrugia KN, Makuc D, Podborska A, Szaciłowski K, Plavec J, et al. 2016. Colorimetric naphthalene-based thiosemicarbazide anion chemosensors with an internal charge transfer mechanism. *Eur J Org Chem* 25:4415–4422. <https://doi.org/10.1002/ejoc.201600509>
107. Byrne S, Mullen KM. 2018. Urea and thiourea based anion receptors in solution and on polymer supports. *Supramol Chem* 30:196–205. <https://doi.org/10.1080/10610278.2017.1394462>
108. Huang H, Xin Z, Yuan L, Wang BY, Cao QY. 2018. New ferrocene-pyrene dyads bearing amide/thiourea hybrid donors for anion recognition. *Inorganica Chim Acta* 483: 425–430. <https://doi.org/10.1016/j.ica.2018.08.055>
109. Sedghi R, Javadi H, Heidari B, Rostami A, Varma RS. 2019. Efficient optical and UV-Vis chemosensor based on chromo probes-polymeric nanocomposite hybrid for selective recognition of fluoride ions. *ACS Omega* 4: 16001–16008. <https://doi.org/10.1021/acsomega.9b02098>
110. Bains D, Singh N, Singh G. 2019. A dipodal thiourea-ionic liquid conjugate system for selective ratio metric detection of HSO<sub>4</sub><sup>-</sup> ion in purely aqueous medium: application by real sample analysis. *Tetrahedron Lett* 60:1457–1462. <https://doi.org/10.1016/j.tetlet.2019.04.029>
111. Li D. 2020. Benzimidazole-isoquinolinone functioned thiourea for selective and reversible recognition of fluoride ion. *J Mol Struct* 1206: 127631. <https://doi.org/10.1016/j.molstruc.2019.127631>
112. Dey SK, Hernández BG, D'Souza M, Mhaldar SN, Gobre VV, et al. 2019. Anion selective disruption of strong intramolecular-NH O=C hydrogen bonds in a nonchromogenic tripodal benzoyl thiourea receptor by display colorimetric response. *Chem Select* 4: 4068–4073. <https://doi.org/10.1002/slct.201803577>
113. So H, Lee H, Lee GD, Kim M, Lim MH, et al. 2020. A thiourea-based fluorescent chemosensor for bioimaging hypochlorite. *J Ind Eng Chem* 89: 436–441. <https://doi.org/10.1016/j.jiec.2020.06.016>
114. Das R, Mahanta S, Talukdar D, Sarma P, Kuliya H, et al. 2021. Colorimetric detection of fluoride ions in aqueous medium using thiourea derivatives: a transition metal ion assisted approach. *Dalbyn Trans* 50: 15287–15295. <https://doi.org/10.1039/D1DT02173G>
115. Kendrick J, Kestenbaum B, Chonchol M. 2011. Phosphate and cardiovascular disease. *Adv Chronic Kidney Dis* 18:113–119. <https://doi.org/10.1053/j.ackd.2010.12.003>
116. Zong Z, Zhang Q, Qu DH. 2023. A single-fluorophore multicolor molecular sensor that visually identifies organic anions including phosphates. *CCS Chem* 1-9. <https://doi.org/10.31635/ccschem.023.202302900>
117. Ritz E, Hahn K, Ketteler M, Kuhlmann MK, Mann J. 2012. Phosphate additives in food—a health risk. *Deutsches Arzteblatt Int* 109: 49–55. <https://doi.org/10.3238/arztebl.2012.0049>
118. Yang S, Li H, Huang Y, Lu A, Wang Z. 2023. A highly selective and sensitive sequential recognition probe Zn<sup>2+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> based on chiral thiourea schiff base. *Molecules* 28: 4166. <https://doi.org/10.3390/molecules28104166>